Progress Report on Performance of A709 and G91 Steels in Sodium

Nuclear Science and Engineering Division

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ABSTRACT

Specimens in six different processing and heat treatment conditions of A709 H58776 were exposed to sodium at 550, 600, and 650°C, respectively for various exposure times. G91 base metal was tested in sodium at 550, 600, and 650°C, and G91 weldment at 550 and 600°C, respectively. Parallel thermal aging experiments were conducted on G91 and A709 to obtain thermal aging data for comparison with sodium exposure results to separate the thermal and sodium effects.

The corrosion data obtained on A709 steel continue to show low corrosion rates, which indicate good compatibility of A709 with sodium when oxygen content is controlled. G91 has also shown acceptable corrosion rates over the temperature range of 550-650°C in sodium.

Thermal aging or sodium exposures reduced the tensile strength, uniform elongation, and total elongation for A709 ESR, AOD specimens. These specimens consistently showed higher yield stress and tensile strength and lower uniform and total elongations after sodium exposure than after thermal aging under comparable testing conditions. It implies that there was an additional effect of sodium exposure that gave rise to an increase in tensile strength of A709. Dynamic strain aging-induced flow serrations were completely removed by either thermal aging or sodium exposure at 650°C, which imply that carbon or nitrogen in solution was removed from the solution and formed precipitates during aging or sodium exposures. The tensile data ruled out the possibility of decarburization under the sodium exposure conditions. The HOMO specimens behaved somewhat differently from the ESR and AOD specimens in sodium.

While thermal aging and sodium exposures at 550 and 600°C decreased the yield stress and the ultimate tensile strength of G91, there was virtually no additional effect resulting from sodium exposures at these two temperatures. In contrast, sodium exposures at 650°C had a drastic effect on the yield stress and the ultimate tensile strength of G91. It is suggested that G91 experienced decarburization in the 650°C sodium environments.

Carbon concentrations in sodium in the SMT-1 and SMT-2 loops were determined by a foil equilibration method. The estimated carbon concentration was in the range of 0.8-1.2 ppm in the SMT-1 loop and 0.3-0.7 ppm in the SMT-2 loop. The carbon activity in sodium in the SMT-2 loop was estimated to be 0.03-0.08 at 600°C, and 0.08-0.2 at 550°C. The carbon activity in sodium at 650°C in the SMT-1 loop was 0.04-0.07.

Equilibrium simulation of the carburization – decarburization processes was conducted for A709 and G91 steels exposed in sodium environments at temperatures of 550-700°C. The carbon activity-concentration relationship for G91 was re-evaluated by considering four phases in G91, i.e. bcc ferrite, $M_{23}C_6$, NbC and VC carbides. It was found that the carburization-decarburization process in G91 steel was dictated by $M_{23}C_6$ carbides at high carbon activities, while NbC carbides dominated the process at low carbon activities. Formation of NbC increases the decarburization resistance of G91 steel. It remains to be understood whether the decarburization resistance provided by MC carbides in G91 can be maintained during long-term operations of SFRs.

The carbon concentration-activity relationship for A709 was calculated based on the equilibrium of fcc-austenite and $M_{23}C_6$ carbide phase. The calculations showed that A709 decarburizes at 650°C in the SMT-1 loop environments, which is different from the experimental findings. The carbon concentration-activity relationship in A709 was further evaluated by considering four phases, including fcc-austenite, $M_{23}C_6$, NbC, and TiC carbide phases. TiC is the most stable carbides among the three carbide phases. The carburization-decarburization process in A709 is dictated by $M_{23}C_6$ carbides at high carbon activities and by TiC at low carbon activities. Formation of TiC increases the decarburization resistance of A709 steel. Because of the complexity of the precipitation process in A709 during sodium exposures, detailed characterization of precipitates in sodium-exposed specimens and improved thermodynamic models are needed to understand the carburization-decarburization behavior of A709. Kinetic analysis of carbon transfer will be investigated for G91 and A709 in future work.

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1 Introduction

The Advanced Reactor Technologies campaign has focused on the sodium-cooled fast reactor (SFR) concept because of its technical maturity. SFRs are also a leading candidate for recycling used fuels to close the fuel cycle. The current needs are for more reliable, more flexible, and more economical reactors suitable for commercial nuclear power generation. Advanced materials are a critical element in the development of next-generation SFRs. Enhanced materials performance not only improves safety margins for component performance and provides design flexibility but is also essential for the economics of advanced SFRs. Advanced Materials Development Campaign focuses on providing the technical basis needed to support the regulatory requirements for structural materials for advanced reactors that could be deployed in the near-to-mid-term by the U.S. nuclear industry. Understanding the compatibility and performance of structural materials in sodium is important for SFR license applications and long-term operations. Research is needed to develop a comprehensive understanding of the effects of sodium environments on the performance of Grade 91 ferritic-martensitic steel and A709 austenitic stainless steel, the lead candidates for SFR applications.

In general, austenitic stainless steels are used for in-core structural components, piping, and intermediate heat exchangers. High-chromium ferritic-martensitic steels are considered for primary piping system, intermediate heat exchangers, secondary piping and steam generators in SFRs. The selection of a particular material or combination of materials used in primary and secondary systems is based upon a number of factors. The stability of a material in the fast neutron environment, compatibility with the sodium coolant and its elevated temperature performance are of primary concern. Degradation due to irradiation, high temperature and stress are common issues to all types of reactor materials, while environmental degradation in sodium is unique to SFR materials.

Structural materials can undergo a variety of interactions upon exposure to liquid sodium. The interactions can be broadly classified into metallic and nonmetallic element transfer. Metallic element transfer is a solution process of a solid metal in liquid sodium. It can cause dissolution of metallic elements into sodium, formation of corrosion products on metallic surfaces, or formation of surface depleted zones. Metallic element mass transfer usually establishes a go/no-go type of evaluation of an alloy for use as a structural material in a sodium environment [1]. Nonmetallic elements, such as oxygen, carbon, and nitrogen, are known to migrate in a material-sodium system as a result of chemical activity differences, under both isothermal and non-isothermal conditions. From the operation of the SFR standpoint, oxygen in sodium can be controlled to ~1 wppm which would result in acceptable corrosion of ferrous alloys at the typical operating temperature [1]. The solubility of nitrogen in sodium is low at the SFR operating temperature and its effect on the materials performance may not be significant [2]. On the other hand, carbon transfer in a material-sodium system can result in carburization or decarburization in an alloy, causing microstructural instability and degradation of its mechanical performance which ultimately affect the lifetime of reactor components [1]. Furthermore, carbon transfer is a dynamic process varying from systems

to systems and cannot be effectively controlled. The influence of carbon in sodium on the microstructure and mechanical properties of structural materials is a major concern for their applications in SFRs.

The objective of this project is to evaluate and understand the influence of sodium environments on the microstructure and mechanical properties of G91 ferritic-martensitic steel and A709 austenitic stainless steel to resolve regulatory and operational issues for extended service in SFRs.

2 Methods

2.1 Materials and Specimens

The first commercial heat 58776 (H58776) of A709 steel was investigated. The composition of H58776 is given in Table 2-1. The melt procedure involved three different processing conditions, namely, Argon-Oxygen-Decarburization (AOD), Electro-Slag Remelting (ESR), and Electro-Slag Remelting with subsequent homogenization (HOMO). Two different heat treatments were conducted on AOD, ESR, or HOMO-processed materials, namely, solution annealed at 1100°C (SA1100°C) for 75 minutes, or solution annealed at 1150°C (SA1150°C) for 60 minutes. Specimens used for sodium exposure tests were fabricated from six different processing and heat treatment conditions listed in Table 2-2.

Two heats of G91 steel were studied, namely, G91-H1 and H30176. Heat G91-H1 was an archive material with a small quantity. 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 heat had a relatively large quantity. It 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 2-3 and 2-4, respectively.

Subsize sheet-type tensile specimens were electrical-discharge-machined with the gauge parallel to the rolling direction. The tensile specimen had nominal gage dimensions of 0.30" × 0.06" × 0.03" and a total length of 1.0". The grip sections of the tensile specimen were extended for 0.2" at each side (shown in Fig. 2-1 [3]), and the extended sections were used for microstructural characterization after sodium exposures. This specimen design ensures that the microstructure and tensile data are obtained on a single sample exposed to the same sodium exposure condition.

G91 weldment specimens were also included in sodium exposure tests. Coupon specimens were machined from the welded plates of G91 H30176 made by Specialty Welding & Machining, LLC., Harrison, TN [4] The nominal dimensions of the coupon specimen were 1.4" × 0.2" × 0.04".

Table 2-1. Chemical composition of melt of A709 first commercial heat, H58776 (wt%)

Fe	C	Cr	Ni	Mn	Mo	N	Si	P	Ti	Nb	B
Bal.	0.066	19.93	24.98	0.91	1.51	0.148	0.44	0.014	0.04	0.26	0.0045

Table 2-2. Processing and heat treatment conditions of A709 H58776.

Processing/heat treatment ID	Processing condition	Solution anneal (SA) temperature (°C)	ANL Lot ID
AOD-SA1100°C	AOD	1100	58776-4-B2
AOD-SA1150°C	AOD	1150	58776-4-C2
ESR-SA1100°C	ESR	1100	58776-3RB-B2
ESR-SA1150°C	ESR	1150	58776-3RB-C2
HOMO-SA1100°C	ESR + Homo	1100	58776-3RA-B2
HOMO-SA1150°C	ESR + Homo	1150	58776-3RA-C2

Table 2-3. Chemical composition of G91 steel (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 2-4. Heat treatment conditions of G91 steel.

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

Figure 2-1. Schematic drawing of a subsize sheet-type tensile specimen (unit in inch) with extended grip sections for tensile testing and microstructural characterization [3].

2.2 Sodium Material Testing Loops

Sodium exposure tests were conducted in two forced convection sodium materials testing loops at the Argonne National Laboratory. The Sodium Materials Test Loop 1 (SMT-1) (shown in Fig. 2-2(a) [5]) consists of a single vessel, an electromagnetic pump, two electromagnetic flow meters, an economizer, and a cold trap. The total amount of sodium in the SMT-1 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 SMT-1 loop has been operating at 650°C.

The Sodium Materials Test Loop 2 (SMT-2) (shown in Fig. 2-2(b) [6]) is a dual sample-vessel loop for sodium exposures at two temperatures. The maximum operating pressure and temperature for the two sample vessels are 5 psig and 700°C, respectively. The total amount of sodium in the SMT-2 loop is approximately 20 kg. The loop is equipped with electromagnetic pumps, electromagnetic flow meters, economizers, and a cold trap. 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. The SMT-2 loop has been operating at two temperatures, with one sample vessel at 550°C, and the other at 600°C.

Both loops are constructed of austenitic stainless steels. The oxygen content of the sodium is controlled by the cold trap method. The temperature of the cold trap is maintained at 125°C to ensure that the oxygen concentration in sodium is at ~1 wppm during specimen exposure [7].

2.3 Sodium Exposure Tests

Specimens in six different processing and heat treatment conditions of A709 H58776 were exposed to sodium at 550, 600, and 650°C, respectively for various exposure times. G91 base metal was tested in sodium at 550, 600, and 650°C, and G91 weldment at 550 and 600°C, respectively. Tables 2-4 and 2-5 summarize the total exposure times at different temperatures for A709 and G91, respectively.

Prior to sodium exposure, each specimen was weighed three times using an OHAUS AP250 analytical balance or Mettler-Toledo XPR26 analytical balance. The thickness of the specimen was measured three times using a micrometer. After sodium exposure, the specimen was removed from the loop, cleaned with alcohol and then with water to remove sodium residues. Specimen surfaces were visually inspected and recorded by a digital camera if needed. Mass and thickness of sodium-exposed specimens were measured to determine the changes in mass and thickness resulting from sodium exposures to estimate the corrosion rates. If only non-destructive measurements (weight and thickness) were performed on a specimen, the specimen was reloaded into the sodium loops for continued exposure.

(a)

(b)

Figure 2-2. (a) Sodium Materials Test Loop 1 (SMT-1) [5] and (b) Sodium Materials Test Loop 2 (SMT-2) [6] at Argonne National Laboratory.

Table 2-5. Sodium exposure temperatures and total exposure times for A709.

Alloy ID	Processing condition	SA Temperature (°C)	Na Exposure Tmperature and Total Exposure Time		
AOD-SA1100°C	AOD	1100	550°C	600°C	650°C
			20,776 h	17,904 h	17,076 h
AOD-SA1150°C	AOD	1150	550°C	600°C	650°C
			20,776 h	17,904 h	17,076 h
ESR-SA1100°C	ESR	1100	550°C	600°C	650°C
			3,311 h	2,976 h	17,076 h
ESR-SA1150°C	ESR	1150	550°C	600°C	650°C
			3,311 h	2,976 h	17,076 h
Homo-SA1100°C	ESR+Homo	1100	550°C	600°C	650°C
			-	-	17,076 h
Homo-SA1150°C	ESR+Homo	1150	550°C	600°C	650°C
			-	-	17,076 h
ESR-SA1150°C + Aging at 775°C			550°C	600°C	650°C
			-	-	3,312 h

Table 2-6. Sodium exposure temperatures and total exposure times for 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	~37,000	~10,000
G91 H30176 weldment	~3,000	~4,700	---

2.4 Thermal Aging Tests

Parallel thermal aging experiments were conducted on G91 and A709 to obtain thermal aging data for comparison with sodium exposure results to separate the thermal and sodium effects. When a material is exposed to sodium at high temperature, thermal aging takes place simultaneously. Therefore, sodium exposure data contain the effects of both sodium exposure and thermal aging. If design factors are developed directly from sodium exposure data, the thermal aging contribution will be accounted for twice as thermal aging factors for yield and ultimate strengths are already implemented in the ASME Code, leading to unnecessary conservatism. Furthermore, to understand the direct effect of sodium on the microstructure and tensile properties, it is important to conduct parallel well-controlled thermal aging tests on the same heats of A709 and G91 steels.

Thermal aging experiments were performed in air furnaces using the same type of specimens shown in Fig. 2-1. Each specimen was wrapped in Ta foil and encapsulated individually in a quartz tube under vacuum. Encapsulated specimens were loaded in an air furnace heated to the target temperature. Thermal aging experiments were conducted at 550, 600, and 650°C on specimens of six different processing-heat treatment conditions of A709 H58776, and on two heats of G91 steel, G91-H1 and H30176.

2.5 Post-Exposure Tensile Tests and Microstructural Characterization

Microstructural characterization and tensile tests were conducted post-sodium or thermal aging tests. The extended grip sections of the tensile specimen were cut from both ends before tensile testing and they were used for microstructural examinations. Metallographic specimens were prepared from the cross section of sodium-exposed or thermally-aged specimens for microstructural characterization by optical microscopy, scanning electron microscopy, and micro-hardness measurements. Thin foil disk specimens of 3-mm in diameter were made for microstructural characterization by transmission electron microscopy (TEM). TEM specimens were electropolished to perforation using a Tenupol twin-jet polishing unit. The electropolishing solution was 95% methanol and 5% perchloric acid cooled to about -40°C.

Sodium-exposed or thermally-aged subsized tensile specimens were tested under uniaxial tension at the sodium exposure or thermal aging temperature to examine the effect of sodium exposure or thermal aging on tensile properties. 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 the analysis of the load and displacement data. All the tests were conducted at a nominal strain rate, 0.001 s^{-1} .

2.6 Measurements of Carbon Concentrations in Sodium Loops

Carbon concentrations in sodium in the SMT-1 and SMT-2 loops were determined by a foil equilibration method. The foil equilibration method requires the material has a low corrosion rate in sodium, a sufficient large carbon diffusivity to reach 99% equilibration in a reasonable time, and a large carbon distribution coefficient between the material and sodium [8]. Pure nickel meets such requirements and was chosen for this application.

Equilibration experiments were conducted using high-purity (99.999%) nickel foils procured from Goodfellow. Foil specimens with a thickness of 0.25 mm were exposed to sodium at 650°C in the SMT-1 loop, and at 600°C in the SMT-2 loop for times necessary to reach 99% of the equilibrium carbon concentration in nickel. The equilibration times were calculated as a function of temperature for nickel foils of various thicknesses [8]. For a nickel foil with a thickness of 0.25 mm, an exposure time of >100 h is required for carbon to reach 99% equilibration at 650°C, and >300 h at 600°C, respectively.

Nickel foil specimens were cleaned by ethanol and water to remove residual sodium after they were removed from sodium loops. The carbon contents in the sodium-exposed nickel foil specimens were measured by a LECO CS844 carbon analyzer to determine the carbon concentration in the foil specimens. The carbon activity and concentration in sodium were estimated as described in [9].

2.7 Thermodynamic and Kinetic Modeling

Equilibrium simulation of the carburization – decarburization processes was conducted for A709 and G91 steels exposed in sodium environments at various temperatures. Thermo-Calc software package was used to calculate the phase diagrams, composition, structure, and volume fraction of equilibrium phases of the alloys using the TCFE9 steel and Fe-alloys database. The database contains thermodynamic properties of steels and many Fe-based alloys required for simulation of the solidification process, the relative stability of matrix phases (austenite and ferrite), precipitation of secondary phases such as sulfides, borides, oxides, phosphides, carbides, nitrides, carbonitrides, and also intermetallic phases such as the sigma and laves phases. Thermo-Calc software was also used to determine the chromium activity coefficients and the carbon concentrations in α -phase in G91 and in γ -phase in A709 to calculate the carbon activity – concentration relationships for these alloys. DICTRA diffusion module can be used to perform carbon diffusion simulations through a wall. DICTRA is based on a numerical solution of multicomponent diffusion equations in various regions of a material with the assumption of local equilibrium at phase interfaces. The carbide precipitation and dissolution processes and the carburization/decarburization rates can be modeled to predict the performance of the steels during service. Simulation of carbon transfer kinetics using DICTRA software package will be reported in future publications.

3 Experimental Results

3.1 Carbon Contents and Activities in Sodium Loops

Table 3-1 summarizes the data of sodium carbon concentration measurements in the SMT-1 and SMT-2 loops. The carbon concentration in sodium, C_{Na} was determined by:

$$C_{Na} = S_{Na} \frac{C_{Ni}}{S_{Ni}} \quad (3-1)$$

where S_{Na} (ppm) is the carbon solubility in sodium, C_{Ni} is the carbon concentration in a nickel foil, and S_{Ni} is the saturated carbon concentration in nickel. Carbon concentrations in equilibrated nickel foil specimens were measured with a LECO CS-844 Carbon Analyzer. The estimated uncertainty was $\pm 5\%$ of the reported value.

The estimated carbon concentration was in the range of 0.8-1.2 ppm in the SMT-1 loop and 0.3-0.7 ppm in the SMT-2 loop. The SMT-2 is a dual-vessel loop, which allows conducting exposure tests at two different temperatures. To measure the carbon concentration in sodium in the SMT-2 loop, all the Ni foil specimens were exposed to sodium at 600°C to ensure that equilibration was reached in a reasonable time. It was assumed that the carbon contents in sodium were the same in the two vessels in the SMT-2 loop. It should be noted that the carbon activity in sodium is dependent on both the carbon concentration in sodium and the carbon solubility in sodium, which changes with sodium temperature [10]. Because of the different temperatures of sodium in the two vessels, the carbon activities in the two vessels were different despite the same amount of carbon in sodium. Figure 3-1 shows the carbon activity as a function of sodium temperature at various levels of carbon contents in sodium. The carbon activity in sodium in the SMT-2 loop was estimated to be 0.03-0.08 at 600°C, and 0.08-0.2 at 550°C. The carbon activity in sodium at 650°C in the SMT-1 loop was 0.04-0.07.

Table 3-1. Carbon concentration measurements in SMT-1 and SMT-2 loops.

Test #	Sodium Loop	Exposure T (°C)	Exposure time (h)	C in Na (ppm)
1	SMT-1	650	1028	0.8
2	SMT-1	650	3066	1.2
3	SMT-1	650	3312	1.0
4	SMT-2	600	1002	0.3
5	SMT-2	600	1294	0.3
6	SMT-2	600	2976	0.7

Figure 3-1. Carbon activity vs. temperature in sodium of various carbon concentrations.

A number of factors can affect the accuracy of measured carbon concentrations and activities in sodium: (1) the sensitivity of a carbon analyzer could lead to uncertainty in the measurements of carbon concentration in equilibrated specimens, particularly for low carbon concentrations in the material; (2) the carbon activity in the nickel foil sample was calculated based on the ratio of the measured carbon concentration and the solubility of carbon in nickel. Literature reported different values of the carbon solubility in nickel, and the carbon concentration in sodium can vary depending on the carbon solubility values used; (3) the carbon concentration in sodium was calculated using the solubility of carbon in sodium that can vary significantly depending on the studies. A factor of about five difference in the solubility values of carbon in sodium has been observed [11].

3.2 Corrosion Behavior

The corrosion data obtained on A709 steel including commercial heat H58776 and development heats continue to show low corrosion rates, which indicate good compatibility of A709 with sodium when oxygen content is controlled. G91 has also shown acceptable corrosion rates over the temperature range of 550-650°C in sodium. Figure 3-2 plots the calculated corrosion rates at three different oxygen contents and the measured corrosion rate data for Grade 91, Alloy 709, and 316H in the SMT-1 and SMT-2 loops [1]. The corrosion rates were calculated using the Monju structural materials design formula [12]:

$$\log_{10} R = 0.85 + 1.5 \log_{10} C_0 - \frac{3900}{(T+273)} \quad (3-2)$$

where R is the corrosion rate (mm/y), C_o is the dissolved oxygen, and T is the temperature (°C). The measured corrosion rates were taken for the exposure times of 10,000 – 30,000 h. It appears that the Monju corrosion formula is valid for both A709 and G91 steels in the sodium environments in the SMT-1 and SMT-2 loops. The estimated corrosion rates for austenitic and ferritic steels 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), respectively at the oxygen level of 1 wppm in sodium.

Figure 3-2. The calculated corrosion rates using the Monju formula and the measured corrosion rate data taken during the exposure times of 10,000 – 30,000 h for G91, A709, and 316H exposed to sodium at 550, 600, and 650°C in Argonne’s forced-convection sodium loops [1].

3.3 Effect of Sodium Exposure on Tensile Properties

Figure 3-3(a) shows the stress-strain curves for the ESR-SA1100°C specimens before exposure, after thermal aging at 650°C for 19,792 h, or after sodium exposures at 650°C for 17,076 h, respectively; Fig. 3-3(b) compares the stress-strain curves for the ESR-SA1150°C specimens before exposure, after thermal aging at 650°C for 19,792 h, or after sodium exposures at 650°C for 17,076 h, respectively. Thermal aging or sodium exposures reduced the tensile strength, uniform elongation, and total elongation for both the ESR-SA1100°C and ESR-SA1150°C specimens. The decrease in tensile strength was less severe under sodium exposure than under thermal aging for both alloy conditions. It implies that there was an additional effect of sodium exposure that gave rise to an increase in tensile strength of A709. Dynamic strain aging-induced flow serrations were observed in the stress-strain curves of the as-received ESR-SA1100°C and ESR-SA1150°C specimens. Flow serrations were completely removed by either thermal aging or sodium exposure at 650°C. Dynamic strain aging is a result of the interactions between free interstitials (e.g. carbon, nitrogen) and dislocations. Because of the high mobility of interstitial

atoms, they segregate to dislocations and cause repeated locking and unlocking of dislocations during plastic deformation, resulting in the serrated flow. The elimination of serrations of the flow curves in A709 H58776 after aging or sodium exposure imply that carbon or nitrogen in solution available for strain aging was removed from the solution and form precipitates during aging or sodium exposures. The tensile data ruled out the possibility of decarburization under the sodium exposure conditions.

Figures 3-4(a) and (b) show the stress-strain curves before exposure, after thermal aging at 650°C for 19,792 h, or after sodium exposures at 650°C for 17,076 h, for the AOD-SA1100°C specimens and AOD-SA1150°C specimens, respectively. The AOD specimens behaved similarly to the ESR specimens.

Figures 3-5(a) and (b) plot the stress-strain curves before exposure, after thermal aging at 650°C for 19,792 h, or after sodium exposures at 650°C for 17,076 h, for the HOMO-SA1100°C and HOMO-SA1150°C specimens, respectively. While thermal aging and sodium exposures showed similar effects on tensile properties of the HOMO specimens to the ESR and AOD specimens, unique characteristics of tensile behavior of the HOMO specimens were observed in the as-received and sodium-exposed conditions. For example, the as-received HOMO-SA1150°C specimen had a much lower yield stress and a low tensile strength than the HOMO-SA1100°C, ESR and AOD specimens. The dynamic straining effect was observable up to the UTS in the HOMO-SA1150°C specimen, while the flow serrations stopped at 20-30% in the rest of specimen conditions before exposure. The flow serrations were also observed in the sodium-exposed HOMO-SA1100°C and HOMO-SA1150°C specimens up to 4-5% strain (shown in the inserts of Figs. 3-5(a) and (b)), while serrations were completely absent in the sodium-exposed ESR and AOD specimens. The fact that the sodium-exposed HOMO specimens showed some flow serrations while flow serrations were absent in the thermally-aged HOMO specimens implies that some fraction of interstitial impurities, e.g. C and N may be retained in solution and precipitation was sluggish under sodium exposures in the homogenization-treated A709.

Figure 3-6 compares the yield stress (YS), ultimate tensile strength (UTS), uniform elongation and total elongation for ESR-SA 1100°C of A709 H58776 after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C, respectively. The ESR-SA 1100°C specimens consistently showed higher yield stress and tensile strength and lower uniform and total elongations after sodium exposure than after thermal aging under comparable testing conditions. Similar observations were made on the ESR-SA 1150°C specimens (Fig. 3-7), the AOD-SA 1100°C specimens (Fig. 3-8), the AOD-SA 1150°C specimens (Fig. 3-9), and the HOMO-SA 1100°C specimens (Fig. 3-10), except the HOMO-SA 1150°C specimens (Fig. 3-11). The HOMO-SA 1150°C specimens had a slightly lower tensile strength after sodium exposure than after thermal aging for ~3kh and 10kh. Dramatic reductions in total elongation of the HOMO-SA 1150°C specimens were observed after sodium exposures for ~10kh and ~17kh.

Figure 3-3. Stress-strain curves for (a) ESR-SA1100°C and (b) ESR-SA1150°C specimens, before exposure, after thermal exposure at 650°C for 19,792 h, and after sodium exposures at 650°C for 17,076 h.

Figure 3-4. Stress-strain curves for (a) AOD-SA1100°C and (b) AOD-SA1150°C specimens before exposure, after thermal exposure at 650°C for 19,792 h, and after sodium exposures at 650°C for 17,076 h.

Figure 3-5. Stress-strain curves for (a) HOMO-SA1100°C and (b) HOMO-SA1150°C specimens before exposure, after thermal exposure at 650°C for 19,792 h, and after sodium exposures at 650°C for 17,076 h.

Figure 3-6. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for ESR-SA 1100°C of A709 H58776. Tensile tests were conducted at 650°C.

Figure 3-7. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for ESR-SA 1150°C of A709 H58776. Tensile tests were conducted at 650°C.

Figure 3-8. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for AOD-SA 1100°C of A709 H58776. Tensile tests were conducted at 650°C.

Figure 3-9. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for AOD-SA 1150°C of A709 H58776. Tensile tests were conducted at 650°C.

Figure 3-10. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for HOMO-SA 1100°C of A709 H58776. Tensile tests were conducted at 650°C.

Figure 3-11. (a) Yield stress (YS), (b) ultimate tensile strength (UTS), (c) uniform elongation and (d) total elongation after thermal aging for 3,144 h, 10,056 h, 19,792 h or sodium exposure for 3,336 h, 10,152 h, 17,076 h at 650°C for HOMO-SA 1150°C of A709 H58776. Tensile tests were conducted at 650°C.

The effect of a sodium environment on tensile properties of G91 is shown in Fig. 3-12 where the yield stress, ultimate tensile strength, uniform elongation and total elongation are plotted as a function of exposure time, respectively for two heats of G91 thermally-aged or sodium-exposed at 550, 600 and 650°C. All the tensile tests were conducted at the exposure temperature. While thermal aging and sodium exposures at 550 and 600°C decreased the yield stress and the ultimate tensile strength of G91, there was virtually no additional effect resulting from sodium exposures. In contrast, sodium exposures at 650°C had a drastic effect on the yield stress and the ultimate tensile strength of G91. Both the yield stress and the 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 in the yield stress and the ultimate tensile strength were >50% after sodium exposures. The effect of thermal exposures at 650°C, on the

other hand, was much smaller, <15% at equivalent exposure times. The reductions of the yield stress and the ultimate tensile strength were accompanied by the recovery of work hardening capacity and the uniform elongation but had minimal effects on the total elongation. Drastic microstructural changes were observed in G91 after sodium exposures at 650°C [13]. It is suggested that G91 experienced decarburization in the 650°C sodium environments.

Figure 3-12. (a) Yield stress, (b) ultimate tensile strength, (c) uniform elongation and (d) total elongation as a function of exposure time for G91 thermally-aged or sodium-exposed at 550, 600 and 650°C, respectively. Tensile tests were conducted at the exposure temperature.

4 Thermodynamic Analysis of Carbon Transfer in Sodium

Carbon is the key element that determines the mechanical properties of steels. The change of the carbon concentration in A709 and G91 during sodium exposure can significantly affect its corrosion rate, microstructural stability, and mechanical properties. The carburization and decarburization behavior of steels depends on both the sodium temperature and the carbon concentration in sodium. Since carbon concentration in a given system is established by a dynamic equilibrium between carbon sources and carbon sinks present in the system, it can vary from system to system as well as over time within the system. Carbon cannot be effectively controlled, unlike oxygen, the level of which can be well controlled by the cold trap method. Therefore, a quantitative understanding and accurate prediction of the carbon transfer in the steel-sodium system is of critical importance for extrapolation of experimental data to the reaction condition and to the safety and reliability of reactor components.

4.1 Carburization-Decarburization Process in G91 Steel

In our previous work [9], the G91 carburization-decarburization boundary was determined through a thermodynamic analysis including two phases, i.e. bcc ferrite and $M_{23}C_6$ carbides. The effect of carbide-forming elements, vanadium and niobium in G91 was not considered. It is known that the microstructure of a normalized and tempered G91 consists of bcc-martensite, $M_{23}C_6$ carbides, vanadium/niobium carbonitrides ($M(Nb,V)X(C,N)$). The carbon activity-concentration relationship for G91 was re-evaluated by considering four phases in G91, i.e. bcc ferrite, $M_{23}C_6$, NbC and VC carbides.

Carbon activity in $M_{23}C_6$ carbide

For the reaction of:

The equilibrium constant K is given as:

$$K = \frac{a_{Cr_{23}C_6}^{1/6}}{a_{Cr}^{23/6} a_C} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4-2)$$

where $a_{Cr_{23}C_6}$, a_{Cr} and a_C are the $Cr_{23}C_6$ activity, Cr activity, and C activity, respectively. The value of formation free energy, ΔG has been reported in several studies. The following expression is based on the average values of the reported enthalpy and entropy data and was used in this study [14]:

$$\Delta G_{Cr_{23}C_6} = -12630 + 2.30T \quad (4-3)$$

where T is the absolute temperature, K, and the unit of ΔG is cal/g-atom C. The equilibrium constant, K can then be expressed as:

$$K = \exp\left(-\frac{-12630+2.30T}{RT}\right) \quad (4-4)$$

where R is the gas constant, 1.987 cal/mol-K.

The $M_{23}C_6$ carbides formed in G91 steel are mixed carbides of $(Fe,Cr,Mo)_{23}C_6$. The $Cr_{23}C_6$ activity in $M_{23}C_6$ carbides was determined by the ideal mixing model. The ideal mixing model assumes that the free energy of mixing in mixed carbides is due entirely to the entropy of mixing of metallic atoms and there are no contributions from carbon and heat of mixing. The activity follows a power relationship with mole fraction in the mixed carbides. The ideal mixing model can be applied to solid solutions of carbides where the metal atoms are similar in size and properties [15]. According to the model, the $Cr_{23}C_6$ activity in $Cr_nM_{(23-n)}C_6$ carbides is given as:

$$a_{Cr_{23}C_6} = \left(\frac{n}{23}\right)^{23} \quad (4-5)$$

where n is the number of Cr atoms in $M_{23}C_6$ carbides. The equilibrium composition of $M_{23}C_6$ in G91 at various temperatures was calculated with Thermo-Calc software and the results are given in [9].

The Cr activity in α -phase in G91 steel, a_{Cr} was calculated with the relations of:

$$a_{Cr} = \gamma_{Cr} X_{Cr} \quad (4-6)$$

where γ_{Cr} is the Cr activity coefficient, and X_{Cr} is the mole fraction of Cr in α -phase in G91. The Cr activity coefficient in α -phase in G91 steel was reported in [9].

The Cr activity in α -phase in G91 steel, a_{Cr} can also be expressed as:

$$a_{Cr} = \gamma_{Cr}^w \cdot [Cr] \\ \text{and } \gamma_{Cr}^w = \gamma_{Cr} \cdot \frac{M_{Cr}}{M_{\alpha}} \cdot 100 \quad (4-7)$$

where γ_{Cr}^w is the Cr activity coefficient in wt%, and $[Cr]$ is the Cr concentration (wt%) in α -phase in G91; M_{Cr} and M_{α} are the molar mass of Cr and α phase, respectively.

At a given carbon activity, a_C , the Cr concentration in α -phase in G91, $[Cr]$ can be estimated by Eqs. (4-2), (4-6) and (4-7). The carbon concentration in $Cr_nM_{(23-n)}C_6$ carbides in G91, $[C]^{M_{23}C_6}$ can then be obtained by:

$$[C]^{M_{23}C_6} = ([Cr]^{tot} - [Cr]) \cdot \frac{12 \times 6}{52 \times n} \quad (4-8)$$

where $[Cr]^{tot}$ is the total concentration of Cr in the steel.

Carbon activity in NbC carbide

For the reaction,

The equilibrium constant K is given as:

$$K = \frac{a_{NbC}}{a_{Nb}a_C} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4-10)$$

where a_{Nb} and a_{NbC} are the Nb activity and the NbC activity, respectively. The value of formation free energy, ΔG can be found in HSC Chemistry. Table 4-1 provides the values of ΔG and K at temperatures of 550 to 700°C.

Table 4-1. Gibbs free energy ΔG and equilibrium constants of NbC at various temperatures.

T (°C)	550	600	650	700
ΔG (kcal/mol)	-32.199	-32.168	-32.138	-32.110
K	3.54×10^8	1.13×10^8	4.07×10^7	1.63×10^7

The Nb activity in α -phase in G91 steel, a_{Nb} can be calculated by:

$$a_{Nb} = \gamma_{Nb} X_{Nb} \quad (4-11)$$

where γ_{Nb} is the Nb activity coefficient, and X_{Nb} is the mole fraction of Nb in α -phase in G91. The Nb activity coefficient in α -phase in G91 steel was determined by Thermo-Calc software.

The Nb activity in α -phase in G91 steel, a_{Nb} can also be expressed as:

$$a_{Nb} = \gamma_{Nb}^w \cdot [Nb]$$

$$\text{and } \gamma_{Nb}^w = \gamma_{Nb} \cdot \frac{M_{Nb}}{M_{\alpha}} \cdot 100 \quad (4-12)$$

where γ_{Nb}^w is the Nb activity coefficient in wt%, $[Nb]$ is the concentration of Nb (wt%) in α -phase in G91, and M_{Nb} and M_{α} are the molar mass of Nb and α phase, respectively.

Assuming the activity of NbC is equal to 1, the carbon activity of NbC can be determined by:

$$a_C = \frac{1}{K \cdot (\gamma_{Nb}^w \cdot [Nb])} \quad (4-13)$$

At a given carbon activity, the Nb concentration in α -phase in G91, $[Nb]$ can be estimated by Eqs. (4-10), (4-12) and (4-13). The carbon concentration in NbC carbides in G91, $[C]^{NbC}$ can then be calculated by:

$$[C]^{NbC} = ([Nb]^{tot} - [Nb]) \cdot \frac{12}{92.91} \quad (4-14)$$

where $[Nb]^{tot}$ is the total concentration of Nb in the steel.

Carbon activity in VC carbide

For the reaction,

The equilibrium constant K is given as:

$$K = \frac{a_{VC}}{a_V a_C} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4-16)$$

where a_V and a_{VC} are the V activity and the VC activity, respectively. Table 4-2 shows the values of ΔG and K at temperatures from 550 to 700°C.

Table 4-2. Gibbs free energy, ΔG and equilibrium constant, K of VC at various temperatures.

T (°C)	550	600	650	700
ΔG (kcal/mol)	-22.628	-22.525	-22.421	-22.314
K	1.02×10^6	4.35×10^5	2.03×10^5	1.03×10^5

The V activity in α -phase in G91 steel, a_V can be determined by:

$$a_V = \gamma_V X_V \quad (4-17)$$

where γ_V is the V activity coefficient, and X_V is the mole fraction of V in α -phase in G91. The V activity coefficient in α -phase in G91 steel was calculated by Thermo-Calc software. Re-write Eq. (18) in terms of the weight percent of V, $[V]$ (wt%), i.e.:

$$a_V = \gamma_V^w \cdot [V] \quad (4-18)$$

$$\text{and } \gamma_V^w = \gamma_V \cdot \frac{M_V}{M_\alpha} \cdot 100$$

where γ_V^w is the V activity coefficient in wt%, and M_V and M_α are the molar mass of V and α phase, respectively.

Assuming the activity of VC is equal to 1, the carbon activity of VC can be obtained by:

$$a_C = \frac{1}{K \cdot (\gamma_V^w \cdot [V])} \quad (4-19)$$

At a given carbon activity, the V concentration in α -phase in G91, $[V]$ can be estimated by Eqs. (4-16), (4-18) and (4-19). The carbon concentration in VC carbides in G91, $[C]^{VC}$ can then be obtained by:

$$[C]^{VC} = ([V]^{tot} - [V]) \cdot \frac{12}{50.94} \quad (4-20)$$

where $[V]^{tot}$ is the total V concentration in the steel.

Carbon concentration – activity relationships

The carbon concentration-activity relationships were calculated for G91 steel over a temperature range of 550 to 700°C, considering three carbide phases, $M_{23}C_6$, NbC, and VC. The composition of G91-H1 and $Cr_{18}Fe_5C_6$ was used in the calculations. The total carbon concentration in G91 at a given carbon activity and sodium temperature was obtained by Eqs. (4-8), (4-14) and (4-20). The carbon concentration in α -phase in G91 was estimated by Thermo-Calc software, and the values were significantly smaller than those in the carbides and can be ignored. The calculated carbon concentrations as a function of carbon activity for G91 are shown in Fig. 4-1 at temperatures of 550, 600, 650, and 700°C. Also shown are the stability of three types of carbides in sodium. It was found that $M_{23}C_6$ carbides were the least stable and the first phase to dissolve in low carbon-activity sodium environments. It dissolves into sodium when the carbon activity is

below 0.005 at 550°C and 0.055 at 700°C. The NbC carbide is the most stable phase among the three types of carbides. It remains stable at a carbon activity as low as 0.001 at 550°C and 0.005 at 700°C. The carburization-decarburization process in G91 steel is dictated by $M_{23}C_6$ carbides at high carbon activities, while NbC carbides dominate the process at low carbon activities. Formation of NbC increases the decarburization resistance of G91 steel.

The thermodynamic analysis shown in Fig. 4-1 indicates that G91 carburizes at 550 and 600°C in the SMT-2 sodium loop environments, which are consistent with the findings of our sodium exposure tests. G91 steel is likely to carburize at 650°C in the SMT-1 sodium loop environments. The experimental data of sodium exposure tests, on the other hand, suggested decarburization of G91 steel in sodium in the SMT-1 loop. Both sodium carbon concentration measurements and calculations of G91 carbon concentration-activity relationship could contribute to this discrepancy.

It should be noted that $M(Nb,V)X(C,N)$ carbonitrides are formed in the normalized and tempered G91 steel. The calculations given in Fig. 4-1 did not account for the formation of NbN and VN, which are thermodynamically more stable than NbC and VC. Figure 4-2 shows the Gibbs free energy of the reactions between carbides (NbC, VC, TiC) and nitrides (NbN, VN, TiN) as a function of temperature. Nitrides of Nb, V, and Ti are more stable than carbides of Nb, V, and Ti in the temperature range of 500-800°C. Detailed characterization is needed to understand the composition of MX carbonitrides in G91. Furthermore, the phase diagram of G91 steel calculated by Thermo-calc software shows that $M(Nb,V)X(C,N)$ carbonitrides are a metastable phase [13]. The MX phase will be replaced by the Z-phase at equilibrium. It remains to be understood whether the decarburization resistance provided by MC carbides in G91 can be maintained during long-term operations of SFRs. Alloy design strategies need to be developed to stabilize MC carbides during extended service.

Figure 4-1. Calculated carbon concentration vs. carbon activity in G91 steel.

Figure 4-2. Gibbs free energy changes as a function of temperature for reactions between carbides (NbC, VC, TiC) and nitrides (NbN, VN, TiN).

4.2 Carburization-Decarburization Process in A709 Steel

Our previous work [16] showed that the solution-annealed A709 had an austenite structure with low dislocation density. Residual MX particles were observed at grain boundaries and within grains. Sodium exposure at 650°C introduced several new phases in A709, e.g. $M_{23}C_6$ carbides, Cr_3Ni_2SiX (X: C, N), and Z-phase precipitates [17]. Table 4-3 shows various equilibrium phases and their volume fraction (vf (%)) formed in A709 at temperatures of 550°C to 700°C. To understand the carburization and decarburization process in A709 in sodium environments, the carbon concentration-activity relationship for A709 was calculated based on the equilibrium of fcc-austenite and $M_{23}C_6$ carbide phase. The carbon activity of $M_{23}C_6$ in A709 steel was determined in a similar manner presented in section 4.1. The calculated carbon concentration-activity relationship is given in Fig. 4-3. The calculations show that $M_{23}C_6$ carbides dissolve when the carbon activity is below 0.2 at 650°C, and A709 decarburizes at 650°C in the SMT-1 loop environments, which is different from the experimental findings.

The carbon concentration-activity relationship in A709 was further evaluated by considering four phases, including fcc-austenite, $M_{23}C_6$, NbC, and TiC carbide phases. The calculation of the activity of TiC in A709 is described below.

For the reaction,

The equilibrium constant K is given as:

$$K = \frac{a_{TiC}}{a_{Ti}a_C} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4-22)$$

where a_{Ti} is the Ti activity and a_{TiC} is the activity of TiC. Table 4-4 shows the values of ΔG and K at temperatures from 550 to 700°C.

The Ti activity in γ -phase in A709 steel, a_{Ti} can be determined by:

$$a_{Ti} = \gamma_{Ti}X_{Ti} \quad (4-23)$$

where γ_{Ti} is the Ti activity coefficient, and X_{Ti} is the mole fraction of Ti in γ -phase in A709. The Ti activity coefficient was calculated by Thermo-Calc software. Re-write Eq. (4-23) in terms of the weight percent of Ti, [Ti] (wt%), i.e.:

$$a_{Ti} = \gamma_{Ti}^w \cdot [Ti] \quad (4-24)$$

where γ_{Ti}^w is the Ti activity coefficient in wt%, and

$$\gamma_{Ti}^w = \gamma_{Ti} \cdot \frac{M_{Ti}}{M_\gamma} \cdot 100 \quad (4-25)$$

where M_{Ti} and M_γ are the molar masses of V and γ phase, respectively.

Assuming the activity of TiC is equal to 1, the carbon activity of TiC can be obtained by:

$$a_c = \frac{1}{K \cdot (y_{Ti}^w \cdot [Ti])} \quad (4-26)$$

At a given carbon activity, the carbon concentration in TiC carbides in A709, $[C]^{TiC}$ is given by:

$$[C]^{TiC} = ([Ti]^{tot} - [Ti]) \cdot \frac{12}{47.87} \quad (4-27)$$

where $[Ti]^{tot}$ is the total Ti concentration in the steel.

The calculated carbon concentration-activity relationships are shown in Fig. 4-4 for A709 steel based on equilibrium of fcc-austenite, $M_{23}C_6$, NbC, and TiC. TiC is the most stable carbides among the three carbide phases. The TiC carbide is stable at a carbon activity as low as 0.001 at 550°C. The carburization-decarburization process in A709 is dictated by $M_{23}C_6$ carbides at high carbon activities and by TiC at low carbon activities. Formation of TiC increases the decarburization resistance of A709 steel. The calculations showed that A709 with the initial total carbon concentration of 0.066% would decarburize initially and then stabilize when the total carbon concentration is reduced to ~0.04%.

Thermodynamic analysis of A709 shows that titanium is preferentially bound with nitrogen to form stable TiN nitrides. Niobium can also be bound with nitrogen to form Z-phase in A709 steel. A majority of carbon atoms will react with chromium to form $M_{23}C_6$ carbides. $M_{23}C_6$ carbides are less stable than TiC and NbC. To increase the stability of A709 in sodium environments, an alloy design strategy is needed to form and maintain TiC and NbC carbides in A709 during long-term service.

Table 4-3. Phases at equilibrium in A709 steel at temperatures of 550-700°C.

		550°C	600°C	650°C	700°C
Phase	Major elements	vf (%)	vf (%)	vf (%)	vf (%)
FCC	Fe, Ni, Cr	82.660	86.534	90.372	94.258
TiN (FCC_A1#2)	Ti, N	0.078	0.078	0.079	0.080
CrN (HCP_A3#2)	Cr, N	1.156	1.142	1.105	1.031
Laves phase	Mo, Fe, Cr	1.802	1.323	0.586	-
$M_{23}C_6$	Cr, Mo, Fe, C	1.341	1.337	1.330	1.319
Sigma	Cr, Fe, Ni	12.350	8.987	5.966	2.786
Z-Phase	Nb, Cr, N	0.462	0.465	0.469	0.473
M_3P	Cr, Fe, P	0.081	0.066	0.040	-
M_2B	Cr, Fe, B	0.069	0.069	-	-
M_3B_2	Mo, Fe, B	-	-	0.055	0.054

Table 4-4. Gibbs free energy ΔG and equilibrium constants of TiC at various temperatures.

T (°C)	550	600	650	700
ΔG (kcal/mol)	-41.835	-41.710	-41.585	-41.457
K	1.28×10^{11}	2.76×10^{10}	7.01×10^9	2.05×10^9

Figure 4-3. Calculated carbon concentration vs. carbon activity in A709 steel based on austenite and $M_{23}C_6$ carbides.

Figure 4-4. Calculated carbon concentration vs. carbon activity in A709 steel based on equilibrium of fcc-austenite, $M_{23}C_6$, NbC, and TiC.

5 Summary

Specimens in six different processing and heat treatment conditions of A709 H58776 were exposed to sodium at 550, 600, and 650°C, respectively for various exposure times. G91 base metal was tested in sodium at 550, 600, and 650°C, and G91 weldment at 550 and 600°C, respectively. Parallel thermal aging experiments were conducted on G91 and A709 to obtain thermal aging data for comparison with sodium exposure results to separate the thermal and sodium effects.

The corrosion data obtained on A709 steel continue to show low corrosion rates, which indicate good compatibility of A709 with sodium when oxygen content is controlled. G91 has also shown acceptable corrosion rates over the temperature range of 550-650°C in sodium.

Thermal aging or sodium exposures reduced the tensile strength, uniform elongation, and total elongation for A709 ESR, AOD specimens. These specimens consistently showed higher yield stress and tensile strength and lower uniform and total elongations after sodium exposure than after thermal aging under comparable testing conditions. It implies that there was an additional effect of sodium exposure that gave rise to an increase in tensile strength of A709. Dynamic strain aging-induced flow serrations were completely removed by either thermal aging or sodium exposure at 650°C, which imply that carbon or nitrogen in solution was removed from the solution and formed precipitates during aging or sodium exposures. The tensile data ruled out the possibility of decarburization under the sodium exposure conditions. The HOMO specimens behaved somewhat differently from the ESR and AOD specimens in sodium.

While thermal aging and sodium exposures at 550 and 600°C decreased the yield stress and the ultimate tensile strength of G91, there was virtually no additional effect resulting from sodium exposures at these two temperatures. In contrast, sodium exposures at 650°C had a drastic effect on the yield stress and the ultimate tensile strength of G91. It is suggested that G91 experienced decarburization in the 650°C sodium environments.

Carbon concentrations in sodium in the SMT-1 and SMT-2 loops were determined by a foil equilibration method. The estimated carbon concentration was in the range of 0.8-1.2 ppm in the SMT-1 loop and 0.3-0.7 ppm in the SMT-2 loop. The carbon activity in sodium in the SMT-2 loop was estimated to be 0.03-0.08 at 600°C, and 0.08-0.2 at 550°C. The carbon activity in sodium at 650°C in the SMT-1 loop was 0.04-0.07.

Equilibrium simulation of the carburization – decarburization processes was conducted for A709 and G91 steels exposed in sodium environments at temperatures of 550-700°C. The carbon activity-concentration relationship for G91 was re-evaluated by considering four phases in G91, i.e. bcc ferrite, $M_{23}C_6$, NbC and VC carbides. It was found that the carburization-decarburization process in G91 steel was dictated by $M_{23}C_6$ carbides at high carbon activities, while NbC carbides dominated the process at low carbon activities. Formation of NbC increases the decarburization resistance of G91 steel. It remains to be understood whether the decarburization resistance provided by MC carbides in G91 can be maintained during long-term operations of SFRs.

The carbon concentration-activity relationship for A709 was calculated based on the equilibrium of fcc-austenite and $M_{23}C_6$ carbide phase. The calculations showed that A709 decarburizes at 650°C in the SMT-1 loop environments, which is different from the experimental findings. The carbon concentration-activity relationship in A709 was further evaluated by considering four phases, including fcc-austenite, $M_{23}C_6$, NbC, and TiC carbide phases. TiC is the most stable carbides among the three carbide phases. The carburization-decarburization process in A709 is dictated by $M_{23}C_6$ carbides at high carbon activities and by TiC at low carbon activities. Formation of TiC increases the decarburization resistance of A709 steel. Because of the complexity of the precipitation process in A709 during sodium exposures, detailed characterization of precipitates in sodium-exposed specimens and improved thermodynamic models are needed to understand the carburization-decarburization behavior of A709. Kinetic analysis of carbon transfer will be investigated for G91 and A709 in future work.

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